Investigation of the light-enhanced emission of mercury from naturally enriched substrates

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Abstract

Incident radiation has been reported to facilitate mercury release from soils. In this study the influence of light on mercury emissions from substrates amended with pure synthetic mercury species, and from naturally and anthropogenically mercury-enriched substrates were investigated using laboratory experiments and in situ flux measurements. Light-enhanced emissions were found to occur from substrates amended with HgS, and from elemental mercury (Hg^0) and $HgCl_2$ amended iron oxide and organic containing substrates. The magnitude of light-enhanced emissions for natural substrates ranged from 1.5 to 116 times that occurring in the dark at the same substrate temperature. Substrates containing corderoite, metacinnabar and "matrix bound mercury" (that bound to organic or inorganic phases) exhibited a higher degree of light-enhanced emissions relative to that containing predominantly cinnabar. Calculated activation energies for both laboratory and field data indicate that photo-reduction is a process associated with the light-enhanced emissions. Activation energies, derived using in situ mercury fluxes and soil temperatures, indicated that photo-reduction was a dominant process facilitating release of Hg from substrates with sunrise. Activation energies, calculated using daytime data, were less than those calculated for sunrise. This is hypothesized to be due to a pool of Hg^0 being developed with photo-reduction at first light that is released as soil temperatures and convective heat transfer increase during the day. This study demonstrated that light energy is the more dominant process controlling mercury emissions from naturally enriched substrates than soil temperature.
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1. Introduction

Mercury (Hg) is naturally enriched in substrates by geologic processes primarily as the mineral cinnabar (HgS), and as impurities in other sulfide minerals such as pyrite (FeS) and sphalerite (ZnS) (Rytuba, 2000). It also occurs naturally as elemental mercury (Hg^0) and organic forms, such as monomethyl mercury and dimethyl mercury, which are bioaccumulated in food webs. Mercury is unique with respect to most other metals because the atmosphere is a very significant pathway by which it is distributed. Mercury in naturally enriched substrate may be released to water or to the atmosphere resulting in local, regional and global distribution, and environmental contamination. Research in the arid west has demonstrated that the atmosphere is the primary pathway by which Hg is released from naturally enriched mine areas (Gustin et al., 2002).

Kothny (1971) pointed out that for any soluble or insoluble Hg compound a measurable amount evaporated. The release of Hg to the atmosphere from HgS has been measured in the laboratory (Karasik and Gerasimova, 1967; Kothny, 1971; Gustin et al., 1997, 1998) and in situ from HgS containing ores during the night and day (Fursov, 1970; Engle et al., 2001; Gustin et al., 2002). One explanation for the release of Hg vapor

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from HgS is that the mineral is thermodynamically stable at high temperatures and reducing conditions and therefore, at low temperatures and oxidizing conditions it could degrade to Hg^0 (cf. Eh–pH diagram in Anderson, 1979). HgS could also be degraded to Hg^0 by microbially facilitated solubilization of Hg(II) simultaneously with oxidation of the sulfide to sulfate and subsequent reduction of Hg(II) to Hg^0 by an enzyme which is present in a number of bacteria (Wood, 1974).

The photo-reactivity of HgS has long been noted in the literature and is readily observed in nature as red HgS turns to black with exposure to light (Kothny, 1971). Baily et al. (1959) suggested that the transformation from red to black was associated with the formation of schuetteite ($HgSO_4 2HgO$) when HgS and H_2O reacted in the presence of sunlight. Davidson and Willsher (1981) and McCormack (2000) demonstrated that blackening of HgS occurred with the simultaneous interaction of light, water and halogens. The blackening of red HgS has also been observed for fresh pieces of HgS ore that have not been exposed to water. Dreyer (1939) suggested that the blackening was due to the development of colloidal Hg^0 produced by the degradation of HgS in light. Other solid Hg phases known to be photo-reactive include: Corderoite—$\alpha Hg_3S_2Cl_2$, Radtkeite—Hg_3S_2ClI, and Kenhsuite—$Hg_3S_2Cl_2$ (Foord and Berendsen, 1974; McCormack et al., 1991; McCormack, 1997). Sulfur and iron complexes have been demonstrated to participate in the photo-reduction of Hg(II) (cf. Stromberg et al., 1991; Lin and Pehknonen, 1997).

Light-enhanced emission of Hg from substrate has been observed in situ (cf. Gustin et al., 1998, 1999; Carpi and Lindberg, 1998; Zhang et al., 2001) and in the laboratory (Gustin et al., 1997, 1998, 1999). Gustin et al. (1997) noted that incident light increased Hg emissions from Hg contaminated mill tailings (Carson River Superfund Site) by 1–2 orders of magnitude above that measured in the dark at the same soil temperature. A significant enhancement in Hg emissions has been reported for a variety of naturally occurring Hg-enriched and background ($<0.1 \mu g \, Hg/g$) substrates in the light relative to that occurring in the dark at the same substrate surface temperature (cf. Engle et al., 2001; Gustin et al., 1999; Zhang et al., 2001). Gustin et al. (1998, 1999), using a controlled laboratory chamber, demonstrated that light-enhanced emissions occurred from substrate amended with pure HgS, from naturally Hg-enriched substrate, and very slightly from substrate amended with Hg^0. They proposed two mechanisms for the light enhancement: photo-reduction of Hg(II) bound up as Fe-oxide or sulfur complexes and/or physical desorption of Hg^0 from substrate. They noted that some photoreactive gas species (i.e. $Hg(SH)_2$ (Stromberg et al., 1991)) could be produced by weathering of HgS.

Understanding the magnitude of emissions from natural substrates is critical for balancing the Hg global biogeochemical cycle, determining if controls on anthropogenic point sources will be effective, and assessing local, regional and global environmental impacts. In order to quantify emissions from naturally and anthropogenically enriched substrates, those factors most important in controlling emissions must be characterized. This paper describes laboratory and field studies designed to investigate the mechanism(s) of light-enhanced Hg emissions from substrate.

This paper presents investigations of light-enhanced Hg emission from substrates amended with synthetic Hg species, and naturally and anthropogenically enriched in Hg. For those substrates naturally enriched in Hg, the phases present were identified in order to see if a link between substrate Hg speciation and light-enhanced emissions could be established. The working hypotheses were that photo-reduction of solid or gaseous Hg phases, and desorption of Hg^0 are mechanisms responsible for the light-enhanced emissions.

2. Materials

Mercury emissions were measured in the laboratory from synthetic Hg chemicals that were amended to ground glass, autoclaved Pyramid Lake sand (3% silt and clay ($<0.064 \, mm$ grain size), 97% sand, and 0.13% organic carbon), ground glass coated with Fe oxide, and a river bank sediment (88% sand, 22% silt and clay, and 3.03% organic carbon) (cf. Sladek and Gustin, 2002) (Table 1). Synthetic Hg species consisted of Red Hg(II)S (Aldrich Chemical 99%), electronic grade Hg^0 (Aldrich Chemical 99.999%), Hg_2Cl_2 (ACS reagent grade 99.6% Sigma) and $HgCl_2$ (Sigma 95%). Soluble species (Hg-chlorides) were added in solution to substrate, which was subsequently dried using a N_2 gas head space. Hg^0 and HgS were added dry to substrates and then ball rolled or shaken to homogenize. A Hg permeation tube (VICI Metronics) was used to generate Hg^0 gas.

Natural and anthropogenic Hg-enriched substrates for which light-enhanced emissions were investigated in the laboratory included: mill tailings from the Carson River Superfund Site (located east of Reno, Nevada (NV), USA) to which Hg^0 liquid was added to extract gold and silver from ore; naturally Hg-enriched substrate and processed mine waste from the Knoxville Mining District (located in central California (CA), USA)), the New Idria Mining District (located in south-central CA), and the Sulphur Bank Superfund Site (located in central CA); and cinnabar (HgS) ore from the Ivanhoe Mining District (located in north-central NV) (Table 2).In situ Hg emissions were measured at the Carson River Superfund Site, the New Idria mining district, the Sulphur Bank Superfund Site, the Ivanhoe

Table 1
Ratio of mercury emissions measured from substrate in the light to that in the dark using the gas exchange chamber and associated activation energies

Substrate	E_a	Conditions	Statistics	Light:Dark
Red Hg(II)S amended to Pyramid Lake sand	10.5	Dark	$R^2 = 0.98$, $p < 0.05$	9.5
	100	Light	$R^2 = 0.99$, $p < 0.06$	
	9.1	Dark	$R^2 = 0.87$, $p < 0.22$	6.3
	82	Light	$R^2 = 0.98$, $p < 0.07$	
Crushed HgS ore amended to ground glass	22.6	Dark	$R^2 = 0.78$, $p < 0.12$	5.6
	149	Light	$R^2 = 0.88$, $p < 0.2$	
Hg^0 amended to Pyramid Lake sand	10.8	Dark	$R^2 = 0.90$, $p < 0.05$	N/A
Hg^0 amended to Fe-oxide coated glass	18.8	Dark	$R^2 = 0.95$, $p < 0.05$	1.35
	55.4	Light	$R^2 = 0.88$, $p < 0.05$	
Hg^0 amended to sediments with 3% organic material	6.7	Dark	$R^2 = 0.97$, $p < 0.07$	1.2
	40.7	Light	$R^2 = 0.98$, $p < 0.09$	
	8.6	Dark	$R^2 = 0.99$, $p < 0.05$	
	42.7	Light	$R^2 = 0.90$, $p < 0.07$	
$HgCl_2$ amended to ground glass	17.3	Dark	$R^2 = 0.98$, $p < 0.05$	N/A
$HgCl_2$ amended to Fe-oxide coated glass	15.7	Dark	$R^2 = 0.95$, $p < 0.11$	9
	16.9	Dark	$R^2 = 0.99$, $p < 0.05$	
	51.3	Light	$R^2 = 0.99$, $p < 0.05$	
$HgCl_2$ amended to sediments with 3% organic material	7.0	Dark	$R^2 = 0.89$, $p < 0.20$	1.3
	28.7	Light	$R^2 = 0.95$, $p < 0.14$	
	5.2	Dark	$R^2 = 0.75$, $p < 0.12$	
	38.7	Light	$R^2 = 0.99$, $p < 0.05$	
Mill tailings from the Parke and Bowie Mill at Carson River Superfund Site	18.9	Dark	$R^2 = 0.99$, $p < 0.05$	18
	152	Light	$R^2 = 0.97$, $p < 0.06$	

Mining District, in the Long Valley Caldera (near Mammoth, CA) and from the Steamboat Springs Geothermal Area (located just south of Reno, NV).

One set of in situ field chamber measurements were made on Hg-amended soils at the Great Basin Environmental Research Laboratory at Desert Research Institute, Reno, NV. The soil was housed in $7.3 \times 5.5 \times 4.5 \, m^3$ ($l \times w \times d$) enclosed chambers or mesocosms (EcoCELLS) designed as open flow mass balance systems (cf. Griffin et al., 1996). Each EcoCELL had three soil containers with ~ 5 tonnes of gravel overlain by ~ 4.5 tonnes soil with a total CELL soil surface area of $11.2 \, m^2$. The soil consisted of a 1:1 ratio of sand and loam amended with mill tailings ($500 \, \mu g \, Hg/g$) from the Carson River Superfund Site to achieve a Hg concentration of $12 \pm 1 \, \mu g/g$. The experimental design of the EcoCELLs allowed for precise manipulation of environmental conditions and measurement of system level response with high resolution. Air temperature within the cells was maintained at constant 26° and 18°C during the day and night, respectively. Incident light and soil surface temperatures were uncontrolled parameters during the daytime for the CELLs were naturally lit. All natural wavelengths of light (measured with an Ocean Optics® Spectrometer) passed through the field chamber in the EcoCELLS. The light intensity in the EcoCELLS was such that visible light was reduced by $\sim 37\%$ and

ultraviolet light by 50% relative to outside. The intensity of ultraviolet light passing through the field chamber, used to directly measure Hg flux from soil, was approximately 5% less than that entering the Eco-CELLs, while the intensity of visible light in the field chamber was $\sim 15\%$ less than that in the EcoCELLs.

2.1. Determination of Hg speciation in substrate

Mercury speciation for some substrates used in the laboratory experiments was determined using a thermal desorption–decomposition method (cf. Biester and Scholz, 1997; Biester et al., 1999), and extended X-ray absorption fine structure spectroscopy (EXAFS) (cf. Kim et al., 2000). The solid phase desorption technique identified Hg minerals and phases in substrates based on comparison of desorption temperatures with those determined for pure Hg minerals or phases. EXAFS entailed the use of high energy X-rays to excite or eject electrons, inducing electronic scattering interactions between the central absorbing atoms and those surrounding (Kim et al., 2000). The scattering patterns are then used in a linear least-square combination analysis to identify the mercury species in substrate based on patterns for known pure compounds. Application of both methods is limited by the high detection limit needed for species identification ($\sim 100 \, \mu g \, Hg/g$), and by

Table 2
Mercury fluxes, total substrate Hg concentration, water-soluble chloride concentration and mercury speciation determined for natural samples used in the gas exchange chamber

Sample location	Sample	Substrate type	Hg flux ng/m²h			Substrate	EXAFS speciation*			Thermodesorption speciation**
			Dark	Light	Light:Dark	µg Hg/g	% HgS	% mHgS	% Other	
Knoxville Mining District-Reed Mine	KMD-R	Mineral soil	919	4666	5.1	131	61	20	19 HgSO₄	Cinnabar with some matrix bound
Knoxville Mining District-McLaughlin South Pit	KMD-M	Crushed ore rock	2795	5066	1.8	267	48	25	28 HgO	Cinnabar with some matrix bound
Knoxville Mining District-McLaughlin South Pit	KMD-M	Crushed ore rock	2583	3122	1.7	267	48	25	28 HgO	Cinnabar with some matrix bound
Knoxville Mining District-Knoxville Mine	KMD-K	Processed ore	480	3741	7.8	135	54	34	12 HgCl₂	Cinnabar with some matrix bound
Carson River Superfund Site-Bessels Mill	CRSS-BM1	Mill tailings	30,496	203,096	6.7	1070				Only matrix bound
Carson River Superfund Site-Bessels Mill	CRSS-BM2	Mill tailings	18,916	116,778	6.2	500				
Carson River Superfund Site-Parke and Bowie	CRSS-PB	Mill tailings	2058	130,726	63.5	217	70	30		Only matrix bound
Idria Mining District-San Carlos Mine	IMD-SC	Waste rock	4093	6200	1.5	527	76		24 HgCl₂	
Idria Mining District-Aurora Mine	IMD-A	Processed ore	35,971	115,828	3.2	468	18	56	26 HgO	
Idria Mining Disrict-Clear Creek Site	IMD-CC	Mineral soil	4074	6475	1.6	130	89		11 HgCl₂	Cinnabar
Idria Mining Disrict-Clear Creek Site	IMD-CC	Mineral soil	589	1215	2.0	130	89		11 HgCl₂	Cinnabar
Idria Mining Disrict-New Idria Mine	IMD-IM	Processed ore	14,018	18,959	1.4	291	64		32 HgSO₄	
Sulphur Bank Superfund Site	SBSS-WR	Waste rock	576	1836	3.2	142				
Sulphur Bank Superfund Site	SBSS-AA1	Altered andesite	376	43,537	115.9	3010				
Sulphur Bank Superfund Site	SBSS-AA2	Altered andesite	737	6028	8.2	2150	20	46	34 Hg₃S₂Cl₂	Mostly cinnabar with trace matrix bound****
Sulphur Bank Superfund Site	SBSS-AA2	Altered andesite	1504	11,152	7.4	2150	20	46	34 Hg₃S₂Cl₂	Mostly cinnabar with trace matrix bound****
Turkey Run Mine-Near Sulphur Bank	SBSS-T	Processed ore	140	909	6.5	1780	58	42		
Ivanhoe Mining District	ID	Crushed cinnabar ore	43,746	110,881	2.5	4560	84		16 HgCl₂	Cinnabar

***Both EXAFS and thermodesorption analysis were not done for the samples used in the lab chamber flux studies.

the availability and overlap of desorption curves and EXAFS spectra for Hg species and phases (Sladek et al., 2002).

2.2. Laboratory measurement of emissions

Mercury emissions were measured under controlled environmental conditions using a laboratory gas exchange chamber (cf. Gustin et al., 1997, 1998, 1999). Experiments were done with pure air generated using an Aadco[®] pure air generator ($0\,\text{ng/m}^3$) for pure Hg phases, and with laboratory air (2–$6\,\text{ng Hg/m}^3$) for natural substrates. Temperature of the air and substrate within the chamber, monitored using thermocouples (OMEGA[®]) and an infrared sensor (Everest Interscience[®]) were averaged and recorded using a data logger (Campbell Scientific[®]). Substrate were introduced to the chamber and allowed to equilibrate for 24 h before experimental manipulations commenced (cf. Gustin et al., 1997). Mercury concentrations at the inlet and outlet of the chamber were measured in 5-min intervals using a Tekran[®] 2537A Cold Vapor Atomic Fluorescence Spectrometer and a Tekran Automated Dual Sampling unit. Measurement of Hg air concentrations in 5-min intervals by this system allowed for assessment of almost real time flux and of the influence of environmental parameters on Hg flux (Gustin et al., 1999a) Mercury flux from substrate was determined using the following equation:

$$F = Q^*(C_o - C_i)/A,$$

where F is the total flux in ng $\text{Hg/m}^2\,\text{h}$; C_o and C_i are the Hg concentration of outlet and inlet air in ng Hg/m^3, respectively; A is the surface area of substrate in m^2; and Q is the flow of air through chamber in m^3/h. Flow of air into the chamber was controlled between 5 and 10 l/min. Chamber blanks, represented by the difference in the Hg concentration of outlet air and inlet air, were measured routinely between experiments and ranged from 0.1 to $0.2\,\text{ng/m}^3$. Reported fluxes represent at least three flux measurements with a coefficient of variation of $<5\%$. For most of the gas exchange experiments a 1–2 mm thick layer of substrate was placed in a petri dish in the chamber. One set of experiments entailed burial of Hg emitting material beneath a 0.5–1 cm layer of quartz sand. Light wavelengths, generated using a Xenon arc lamp, transmitted through the Pyrex chamber were $>500\,\text{nm}$ determined using an Ocean Optics[®] Spectrometer. Light intensity was adjusting using the voltage to the lamp and the light-driven emissions were compared to those in the dark at the same surface temperature at the highest light intensity ($600\,\mu\text{mol/m}^2\,\text{s}$). Light intensities were varied to investigate the influence of light on flux at 40, 200 and $600\,\mu\text{mol/m}^2\,\text{s}$ measured with a Li-Cor 250 quantum sensor.

2.3. In situ measurement of mercury emissions

In situ Hg emissions reported in this study were measured using a cylindrical polycarbonate field flux chamber with a radius of 10 cm, a height of 3.5 cm, and a 1 l volume (cf. Engle et al., 2001; Gustin et al., 2002) or with a Modified Bowen Ratio micrometeorological method (cf. Lindberg et al., 1995; Meyers et al., 1996; Gustin et al., 1999a), and a Tekran (Model 2537A) CVAFS–TADS system. Mercury flux for the field chamber measurements was calculated using the same equation described above for the laboratory chamber. The chamber flow was controlled between 5 and 10 l/min. Coincident with the measurement of Hg flux, air and substrate temperature (OMEGA[®] thermocouples), and incident light (Li-COR[®] LI200x) were averaged and recorded for 5-min intervals using a data logger (Campbell Scientific[®] CR21X). As mentioned, both visible and ultraviolet wavelengths of light passed through the field chamber.

Total Hg concentration of substrates was determined using cold vapor atomic absorption spectroscopy after aqua regia digestion (Lechler, 1999). Statistical analyses of data were done using STATVIEW (SAS Institute, Inc.).

3. Results and discussion

3.1. Amended substrates

Detectable amounts of mercury were constantly emitted from all synthetic Hg species (HgS, $HgCl_2$, Hg_2Cl_2 and Hg^0) in the dark and light. Of the pure synthetic Hg species amended to quartz sand, HgS was the only species that exhibited light-enhanced emissions above that occurring in the dark at the same substrate temperature (Table 1). Gustin et al. (1998) reported similar results. Emissions from natural (Ivanhoe cinnabar ore) HgS at $40°C$ in the light ($1 \pm 0.5\,\text{ng/cm}^2\,\text{h}$) and dark ($0.1 \pm 0.02\,\text{ng/cm}^2\,\text{h}$) occurred continuously (measured over 48 h) within the gas exchange chamber. Emissions from HgS were enhanced by 6–10 times immediately with incident light and returned to dark emission rates as soon as light exposure ceased.

In order to determine if Hg bound to iron oxides and organic matter in substrate would be released through photo-induced desorption of Hg^0 or photo-reduction, experiments were done using $HgCl_2$, Hg^0 and Hg_2Cl_2 amended to iron oxide and organic containing substrates. Light-enhanced emissions above that occurring in the dark at the same surface temperatures were observed for all substrates except those containing Hg_2Cl_2 (Table 1).

For those substrates exhibiting light-enhanced emissions, Hg flux increased as a function of increasing light

intensity (Table 1; Fig. 1). The slope of the curve describing the logarithm (log) of Hg flux as a function of temperature in the dark for the synthetic HgS amended substrate ($m = 0.021$, $p < 0.05$, $r^2 = 0.98$) was significantly less than that describing the log of Hg flux and soil temperature at different light intensities ($m = 0.188$, $p < 0.05$, $r^2 = 0.97$) and slightly less than that describing the slope of the vapor pressure curve for Hg of 0.035 (cf. Gustin et al., 1997). The slope of curves describing the log of emissions from Hg^0 amended organic containing sand and $HgCl_2$ amended Fe oxide and crushed HgS ore in the dark roughly paralleled the slope of the curve describing the vapor pressure for Hg^0 (Fig. 1). This was also observed for emissions from Hg

contaminated mill tailings in the dark (Gustin et al., 1997). This suggests that in the dark solid Hg phases constantly release Hg^0 through chemical deterioration.

A useful parameter for understanding the processes involved in volatilization or the release of Hg from substrate is the activation energy. The activation energy (E_a) is calculated using the Arrhenius equation:

$$\ln K = \ln A - (\Delta H / RT),$$

where A is a frequency factor or the number of times the atoms are close enough to react, ΔH is the E_a or molar heat of vaporization (kcal/mol), T is the absolute temperature ($^\circ$K) and K is a rate constant which may be equated with Hg flux measured at specific temperatures (cf. Lindberg et al., 1979, 1995; Gustin et al., 1997; Carpi and Lindberg, 1998; Zhang et al., 2001). The E_a for the volatilization of Hg^0 liquid is 14 kcal/mol at 25°C (Lide, 1993). The E_a calculated for synthetic HgS and Hg^0 amended Pyramid Lake Sand in the dark was slightly less than the E_a for the vaporization of Hg^0 liquid. This may be due to a higher temperature range used to generate the data for the E_a calculated in Table 1 (27–42°C). Natural HgS ore had a higher E_a calculated for emissions in the dark than the pure HgS. This is most likely due to the fact that the HgS ore was made up of dense silica and cinnabar, whereas the synthetic HgS was a pure fine powder. For $HgCl_2$ and Hg_2Cl_2 amended sand the calculated $E_a s$ were higher (20–25) than that for volatilization of Hg^0 in the dark indicating that the more oxidized chloride species are not as readily degrading to Hg^0 as the more reduced forms. The E_a calculated using substrate temperature, adjusted by varying light intensity, and Hg flux for the pure and natural HgS containing substrates were significantly higher than E_a for Hg^0 volatilization indicating that additional energy was being consumed in the process of releasing Hg^0, and that photo-reduction was occurring (Table 1).

To investigate whether gaseous Hg species or Hg^0, derived from solid Hg phases and moving up through substrate, were being photo-reduced or desorbed, respectively, upon interaction with light at the air:soil interface, emissions were measured from Carson River mill tailings, crushed HgS ore and a Hg^0 permeation tube buried beneath clean quartz sand. Emissions of Hg constantly occurred from the buried material indicating that Hg vapor was constantly being produced and migrating towards the air–substrate interface. No enhanced emissions were observed with incident light indicating that photo-reduction of gaseous phases, such as $Hg(SH)_2$, being emitted from the buried materials was not occurring (Fig. 1).

To address the hypothesis of Gustin et al. (1998), that Hg^0 migrating from depth and oxidized and bound to iron oxides at the air:surface interface is subsequently released by photo-reduction, 3 experiments were done using the same buried materials above. For each, a layer
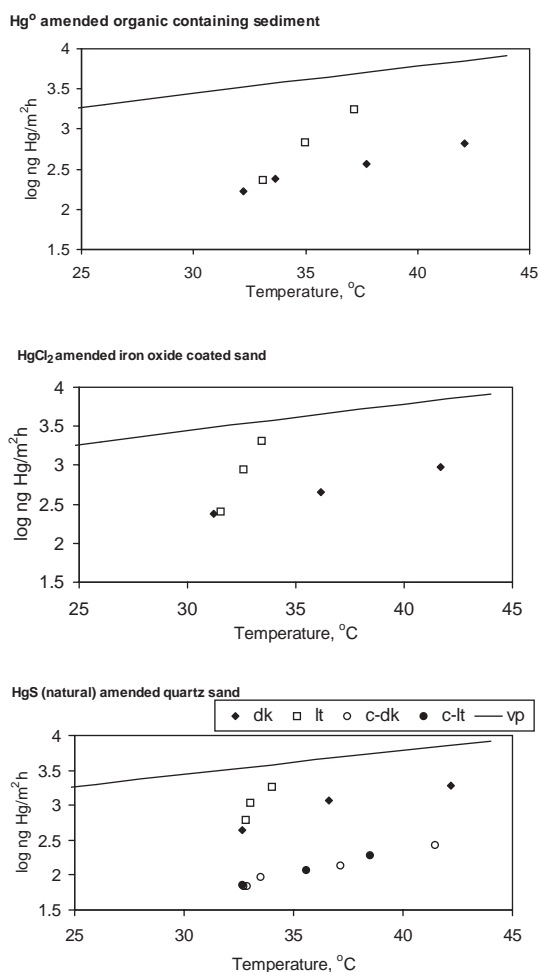

Fig. 1. Logarithm of mercury flux from amended substrates as a function of temperature in the light (lt) and dark (dk). Light data was obtained by adjusting light intensity and dark data by manipulating temperature. Flux was also measured from natural HgS covered (c) with a layer of sand in the dark (c-dk) and in the light (c-lt). Also shown is the line for the vapor pressure curve for elemental mercury (vp).

of iron oxide coated quartz was placed on top of the quartz sand beneath which was the gaseous Hg emitting material. No light-enhanced emissions were observed. In one experiment the layered substrate (Hg permeation tube, quartz sand, iron oxide coated quartz) was placed in a fume hood for a week providing for interaction of the Hg^0, Fe oxide and ambient lab air. No light enhancement of emissions was observed for subsequent exposures in the gas exchange chamber.

These experiments indicated that HgS, as well as $HgCl_2$ and Hg^0 liquid amended to iron oxides and organic containing substrates participate in photo-induced emissions of Hg from substrate. Interaction of Hg^0 gas with iron oxides does not elicit the same response as Hg^0 liquid.

3.2. Natural substrates

All natural samples used in the gas exchange chamber exhibited light-enhanced emissions of Hg with incident radiation relative to that occurring in the dark at constant substrate temperature (Fig. 2a) Note that emissions have been normalized based on the Hg concentration in the substrate). The ratio of Hg flux in the light to that in the dark at 35^0 ranged from 1.4 to 116 with the highest ratios associated with the Park and Bowie tailings sample and altered andesite from Sulphur Bank Superfund Site (Table 2). Light-enhanced emissions were measured from duplicate samples from the Knoxville District (KMD-M), New Idria District (IMD-CC) and Sulphur Bank (SBSS-AA2) and the same degree of light enhancement was measured (Fig. 2b, Table 2). Light-enhanced emissions were measured from samples taken from two different locations at the Bessel Mill tailings and the same degree of light enhancement was observed (Table 2). Gustin et al. (1999) reported a similar range in the light-to-dark ratio of Hg emissions at constant temperature for substrate collected from the Steamboat Springs Geothermal area, south of Reno, NV, the Clyde Forks Mineralized Fault Zone, Ont., Canada, Proterozoic Black Shales from Canada, and the Carson River Superfund Site, NV. They found that light-enhanced emissions from tailings from the Carson River Superfund site were highest, being 14.5 times greater than those in the dark at the same temperature. For the other substrates light emissions were 1.1–4 times greater than those measured in the dark at the same surface temperature.

The Hg speciation in substrate used was investigated to see if this would explain the variability in the amount of light enhancement. No Hg^0 was identified by thermodesorption in any samples and EXAFS cannot identify Hg^0. Sladek et al. (2002) through selective extractions found $<0.7\%$ volatile Hg in some of the samples used in this study. Considering the high concentration of Hg in the natural samples used in this
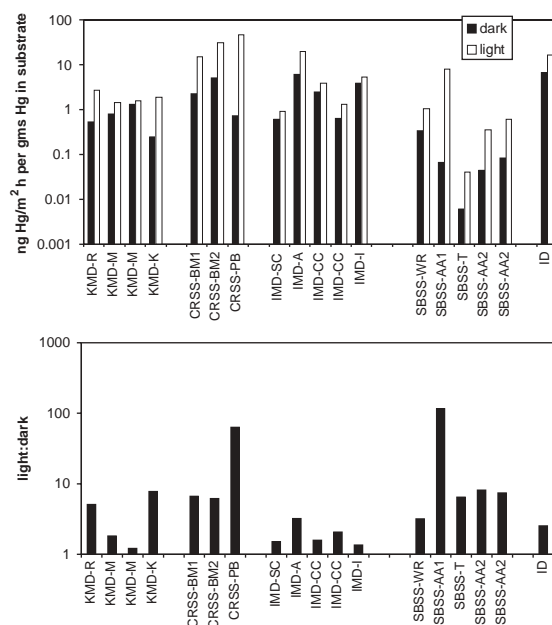

Fig. 2. (a) Histogram showing Hg flux measured in the light and dark from natural samples at 35°C normalized to the total mercury concentration in substrate using the gas exchange chamber. (b) Histogram showing light:dark ratio at 35°C of mercury emissions for natural samples measured using the gas exchange chamber.

study, samples could contain 100–10 s of thousands of ng of Hg^0, so its presence and release cannot be ruled out. In general, natural substrates identified by EXAFS as having $>65\%$ combined HgS and metacinnabar (mHgS) exhibited a higher degree of light enhancement (light:dark flux ratio >3) than samples having primarily cinnabar or a lesser amount of cinnabar and mHgS combined (1.4–3 times greater emission in light). Samples for which thermodesorption analysis identified matrix bound Hg, which includes Hg bound to iron, sulfur and organic phases, and mHgS, exhibited a higher degree of light-enhanced emissions than those identified as having predominantly cinnabar.

Samples of rock material and soil from the New Idria mining district (IMD), for which cinnabar was identified by EXAFS as the predominant mineral, had the lowest light-enhanced emissions of all the samples. A calcine sample (processed Hg ore) from Aurora Mine (IMD-A), identified by EXAFS as having HgO and mHgS, exhibited a higher degree of light-enhanced emissions relative to other samples from the district. The ratio for light:dark emissions for substrate from New Idria district were less than that found for pure HgS amended sand (6–10) (Table 1). Both EXAFS and thermodesorption identified cinnabar as the predominant Hg phase in

the Clear Creek soil (IMD-CC) for which light-enhanced emissions were about 1.6 times that measured in the dark, significantly less than that obtained for pure synthetic HgS and for finely crushed cinnabar ore (Table 2). This difference is most likely due to the fact that the pure HgS consisted of a fine powder and the HgS ore was crushed, while the natural samples consisted of aggregates of minerals with Hg species not as available for interaction with light.

Those samples containing mHgS and cinnabar as identified by EXAFS exhibited a significantly greater degree of light enhancement than those samples with only HgS identified. Thermodesorption analysis identified matrix bound Hg in all samples that EXAFS analysis identified mHgS. It is possible that the matrix bound Hg is mHgS because Biester et al. (2000) presented a Hg release curve for mHgS that overlapped the temperature range where matrix bound Hg is released. Although mHgS is considered the high temperature form of HgS that will transform to cinnabar at 1 bar 344°C (Dickson and Tunnell, 1959), it is produced in the laboratory and in natural environments at low temperatures (Pacquette and Helz, 1997; Barnett et al., 1997; Ravichandran et al., 1999). Metacinnabar, whether a high or low temperature form is the less stable form of HgS, and this perhaps would facilitate the photo-induced production and release of Hg^0 from this phase.

Mill tailings samples from the Carson River Superfund site, where Hg^0 liquid was anthropogenically amended to substrate, exhibited a significantly higher Hg flux response to incident light than most other natural substrates. Mill tailings from the Carson River Superfund site were identified as having primarily matrix bound Hg by thermodesorption analysis, and cinnabar and mHgS by EXAFS (Table 2). Sladek and Gustin (2002) found, using back-scatter and energy dispersive X-ray analysis, that Hg was associated with silver–sulfur, iron–sulfur, gold–silver and sulfur containing phases. The high light-enhanced response seen with tailings samples may be due to the photo-reduction of Hg in these phases. In addition, the high surface area of the tailings, which consisted of predominantly silt and clay-sized grains, could have further exacerbated the response. Mill tailings from the Parke and Bowie Mill consistently exhibited a higher degree of light-enhanced emissions than those from Bessel Mill. The difference in the degree of light-enhanced emissions between substrate from the two mill tailings sites is perhaps an artifact of differences in ore processing. Bessel Mill was a site of primary ore processing while the Park and Bowie Mill was a site of tailings reprocessing (Anasari, 1989). Reprocessing could have further depleted the primary ore mineral, argentite (AgS), in Ag and resulted in increasing S sorption sites for Hg, perhaps forming mHgS.

The highest light-enhanced Hg emissions occurred from altered andesite taken from the Sulphur Bank mine open pit. Although EXAFS and thermodesorption analysis were not performed for the exact samples used in the gas exchange chamber, EXAFS analysis has identified the mineral $Hg_3S_2Cl_2$ in samples from Sulphur Bank (Kim et al., 2000). Corderoite is a photo-reactive Hg species (McCormack, 2000).

Fig. 3 illustrates the light-enhanced emissions of Hg measured in the gas exchange chamber as a function of time at constant temperature for several natural samples. For each there was an initial pulse of Hg released with the first light and then the emissions remained higher than they were in the dark. As seen with
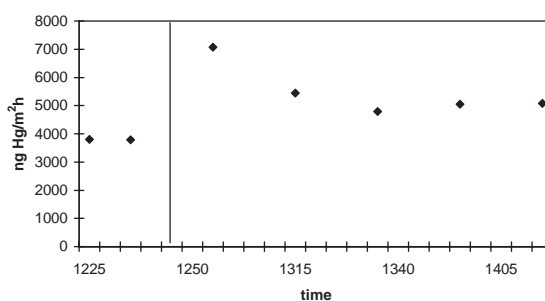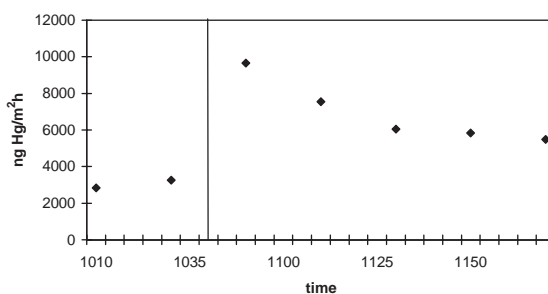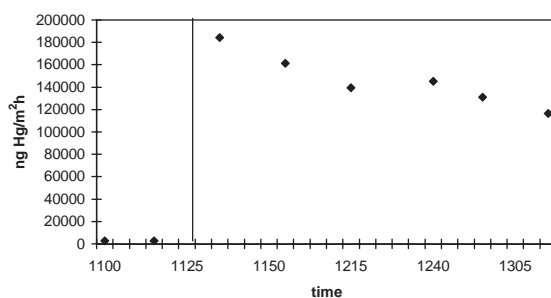

Fig. 3. Graphs illustrating the effect of light on emissions from three natural samples measured in the gas exchange chamber with soil temperature maintained at $35 \pm 1°C$. Vertical line indicates when the light was turned on.

Table 3
Slope of the line describing the relationship between the logarithm of Hg flux versus temperature and activation energies for natural samples measured with the gas exchange chamber

Location	Sample	Condition	Log flux v temperature			Activation energy		
			Slope	r^2	p	E_a	r^2	p
CRSS-PB	Mill tailings	Dark	0.02	0.99	0.08	10.60	0.97	0.07
KMD-M	Processed ore	Dark	0.03	0.98	0.08	12.40	0.97	0.07
KMD-R	Crushed ore rocks	Dark	0.07	0.98	0.08	31.60	0.95	0.10
SBSS-AA2	Altered andesite	Dark	0.07	0.29	<0.07	30.00	0.29	0.07
SBSS-AA2	Altered andesite	Light	0.12	0.98	<0.05	47.00	0.98	<0.05
IMD-CC	Mineral soil	Dark	0.05	0.76	<0.05	17.50	0.84	<0.05
IMD-CC	Mineral soil	Light	0.11	0.90	<0.05	54.40	0.99	<0.05

the synthetic samples, emissions for the natural samples increased as a function of temperature in the dark. Table 3 gives the slopes of the lines describing log of Hg flux as a function of temperature in the dark for several anthropogenically altered substrates, which were less than that for the Hg^0 vapor pressure curve, and for two natural samples, which exhibited slopes greater than that for the Hg^0 vapor pressure curve. The E_a for several natural samples, calculated using fluxes measured in the light (Table 3), were significantly greater than that needed for the conversion of Hg^0 liquid to vapor (47 and 54). Using data from Gustin et al. (1998), the E_a calculated for flux in the light from mill tailings from the Carson River Superfund Site, NV was 75 kcal/mol and for cinnabar ore, from the Ivanhoe mining district, NV, 66.8 kcal/mol. These high E_a associated with Hg flux in the light from natural substrates indicate that photo-reduction was occurring.

3.3. In situ measurement of emissions

Fig. 4 illustrates the light-enhanced emissions observed in situ with initial light from soils within the Long Valley Caldera near Mammoth, CA, the New Idria Mining District-Clear Creek Site (IMD-CC), and from altered andesite at the Sulphur Bank Superfund Site, CA (SBSS-AA2). In the Long Valley Caldera it was quite cold and the soil temperature changed little with sunrise. Mercury emissions increased briefly with initial light at 700 h and then declined only to increase dramatically when sunlight was directly incident on the site. At Clear Creek, Hg flux increased dramatically with first light flux with no change in soil temperature. At Sulphur Bank Hg flux increased simultaneously with soil temperature and light intensity making it more difficult to separate out the effects of light versus temperature. For the Clear Creek and Long Valley data, the statistical correlation between flux and light was greater than the correlation between flux and temperature (Fig. 4). Using stepwise regression, 73.9% of the variability in flux at Long

Valley was explained by light with an improvement to 74.0% and 74.6% ($p < 0.0001$) with the addition of soil temperature and relative humidity to the analysis. At New Idria light explained 52.3% of the flux variability with no improvement with the addition of soil temperature data. At Long Valley flux measurements were made in the spring, where as at New Idria measurements were made in the fall. Sulphur Bank field data was collected in the summer and regression coefficients for both light and temperature with Hg flux were very high and similar. This suggests that under conditions of high temperatures and high light intensity both factors significantly influence emissions.

Fig. 5 shows Hg flux, light intensity and soil surface (1–5 mm) temperature measured using a field chamber on the surface of one of the soil containers in an EcoCELL at Desert Research Institute from 17 to 21 November 2000. This figure illustrates how Hg flux responds rapidly to fluctuations in light accompanied by small to little change in soil temperature. As light intensity decreased from the 17th to the 21st, the maximum daily Hg flux declined, however, soil temperature remained approximately the same. The relationship between incident light and flux ($r^2 = 0.75$, $p < 0.0001$) was better than that between flux and soil temperature ($r^2 = 0.57$, $p < 0.0001$) and water vapor flux measured as $\mu mol/m^2$ s ($r^2 = 0.202$, $p < 0.0001$). Stepwise regression analysis revealed that 75.1% of the variability in flux could be explained by light with the addition of soil temperature improving this to 77.5% and H_2O vapor flux to 80.1% ($p < 0.0001$). The E_a calculated for daytime data were higher than those calculated for nighttime data for all days but the most cloudy at the end of the week. This indicates that photo-energy was important in supplying Hg^0 that could be released over time. Calculated E_a for the night-to-day transition were greater than that calculated for daytime data. This suggests that during the night-to-day transition photo-reduction was an important process producing Hg^0 that is available for subsequent release during the
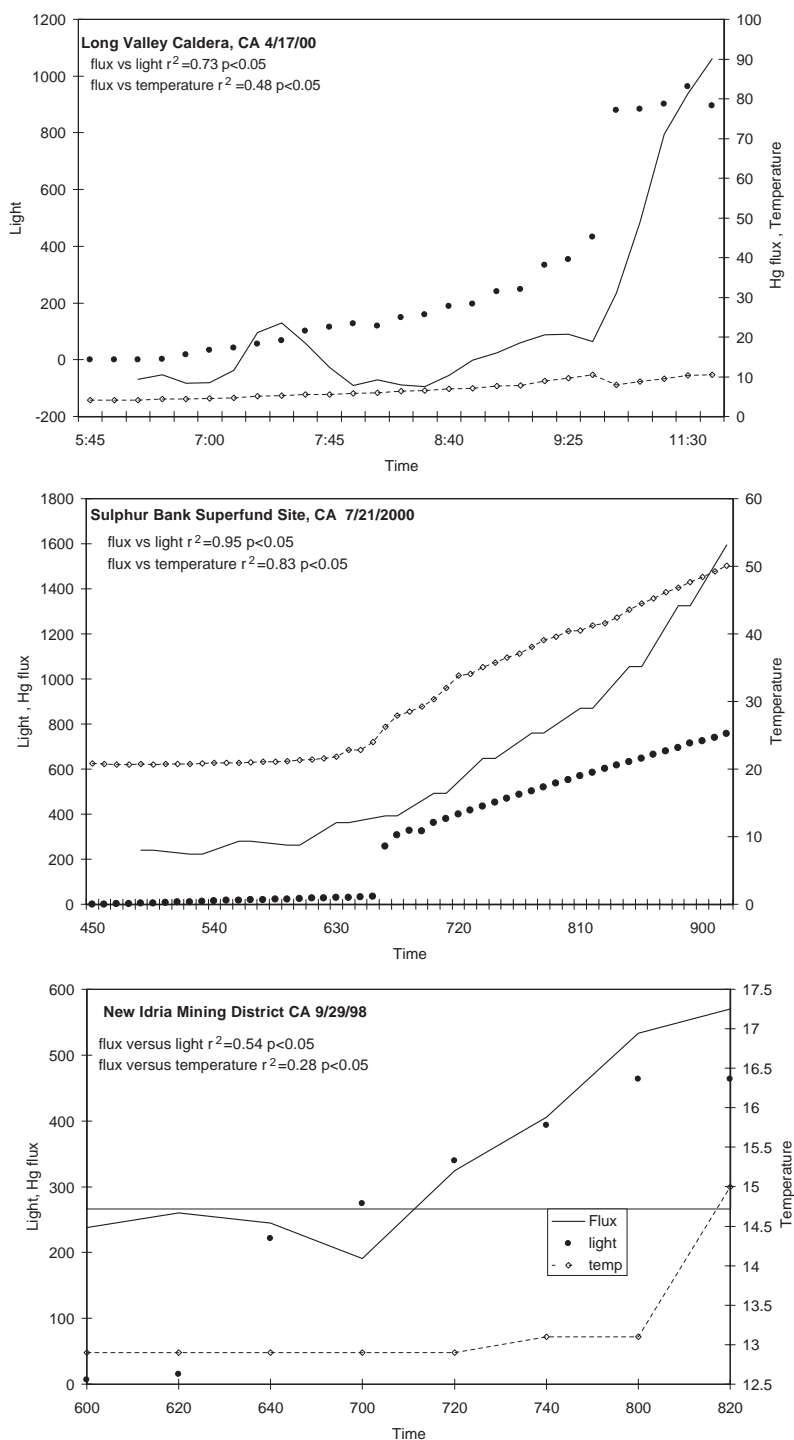
Fig. 4. Graphs illustrating the influence of first light on in situ mercury emissions.

day. This production of a pool of Hg^0 early in the day that would be available for subsequent release during the day, could explain the reduced daytime activation energies.

E_a were calculated using Hg flux and soil temperature collected in situ at six field sites (Table 4). For all field sites, with the exception of Long Valley, the $E_a s$ calculated using fluxes measured after sunrise were less
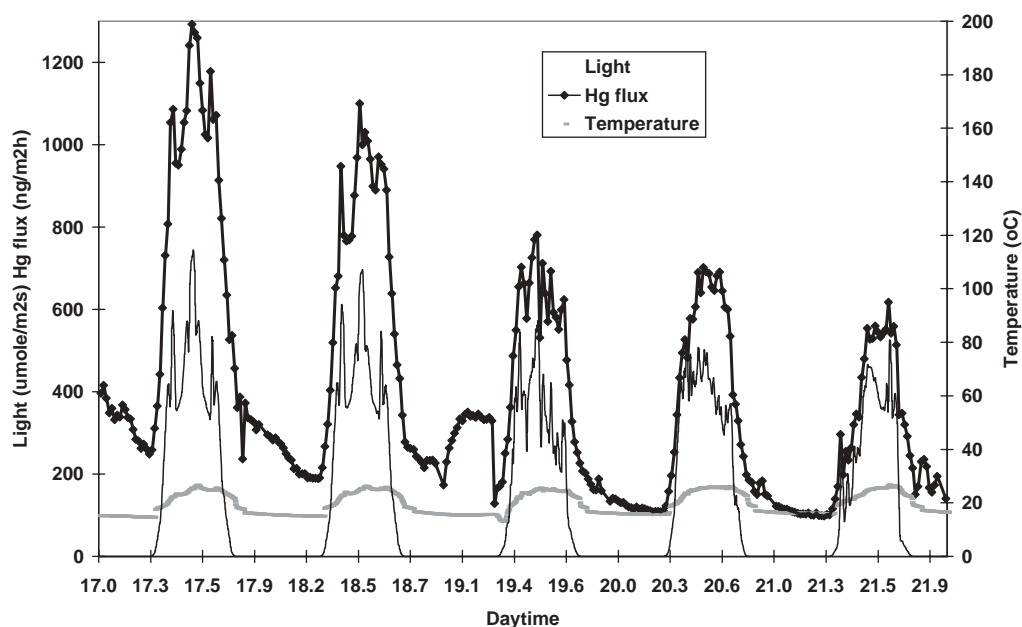
Fig. 5. Mercury flux versus time measured using a field chamber in the EcoCELLs at Desert Research Institute. Also shown are soil temperature and light intensity.

than the E_a for the volatilization of Hg^0. Activation energies calculated using Hg fluxes and temperatures for sunrise were greater than that needed for the volatilization of Hg^0, except for Steamboat Springs and Sulphur Bank. At Sulphur Bank and Steamboat Springs the E_a calculated for all time periods was less than that for Hg^0 volatilization. This is most likely due to the fact that both these areas are geothermally active and crustal heat flux is an important parameter driving Hg movement across the substrate:air boundary (Gustin et al., 2002). It is noteworthy that the E_a calculated for the night-to-day transition for the Clear Creek site E_a (71 kcal/mol) was similar to that determined for the same soil using the gas exchange chamber (54 kcal/mol). The lower value for the gas exchange chamber may reflect the fact that no ultraviolet light passed through the gas exchange chamber whereas it did pass through the polycarbonate field chamber. Zhang et al. (2001) demonstrated that reduction of ultraviolet light lowered the light-enhanced emissions by ~24%.

The high E_as calculated for the night-to-day transition suggest that with initial light photo-reduction is a dominant process controlling emissions whereas as the day progresses release of photo-produced Hg^0 becomes the major mechanism of Hg release. Carpi and Lindberg (1997) measured light-enhanced emissions from sewage sludge and concluded, based on the fact that the E_a for emissions in the light (26.2 kcal/mol) was higher than that associated with a shaded chamber (22.6 kcal/mol), that in situ reduction must be occurring. Activation

energies based on in situ data from sites with background Hg concentrations in substrate (Table 4) are also higher than the value for simple volatilization of Hg^0 indicating that photo-reduction of Hg containing phases may be important. At background sites the pool of Hg for photo-reduction will be much less than that at naturally enriched sites, which were the focus of this study. Because of this, a build up of Hg^0 will not occur in the soil so a reduction of the apparent activation energy during the day may not be realized.

4. Conclusion

Light is a dominant process controlling Hg emissions from substrate. The response of Hg flux to fluctuations in incident radiation is immediate and continuous over time. Regression analyses of in situ measured Hg fluxes versus light and temperature demonstrate that light is a more important parameter controlling emissions than temperature. The dominant role of light was also demonstrated by the data collected within the Eco-CELLS over 5 days during which Hg flux and incident radiation declined but soil temperatures remained the same.

Light wavelengths in both the visible and ultraviolet realm appear to play a role in the light-enhanced emission of Hg from substrate. Light-enhanced emissions were measured from substrate exposed in the lab chamber where only light in the visible realm was

Table 4
Activation energies calculated using in situ derived mercury fluxes and soil temperature

Location/sample date	substrate μg Hg/g	Method	Sunrise	Calculated E_a		
				Time	E_a	Statistics
New Idria Mining District, Clear Creek Site, CA 9/98	Soil Site 1 = 125 μg/g Site 2 = 49.2 μg/g	FC	600	Site 1 600–820 700–1200 Site 2 6–820	71 6 60	$r^2 = 0.45$, $p < 0.05$ $r^2 = 0.50$, $p = 0.05$ $r^2 = 0.44$, $p = 0.07$
Ivanhoe mining distrct, NV 9/98	Soil 0.06 μg/g	FC	540	Night 600–1000 Day	23 16 7	$r^2 = 0.51$, $p < 0.05$ $r^2 = 0.74$, $p < 0.05$ $r^2 = 0.35$, $p < 0.05$
Gold Hill, Carson River Superfund Site, NV 8/99	Reprocessed tailings 0.18 to 0.43 μg/g	UMet	500	31 July 330–1000 1 August 330–1000	20 31	$r^2 = 0.45$, $p < 0.05$ $r^2 = 0.59$, $p < 0.05$
Steamboat Springs Geothermal Area, NV 10/98	Soil 3–5 μg/g	UMet	700	Day and night data < 14 kcal/mol Day night transition ⩽ 14		
Long Valley Caldera, NV 4/00	Soil 0.023 μg/g	FC	625	700–1130	70	$r^2 = 0.28$, $p < 0.05$
Sulphur Bank Superfund Site, Clearlake, CA 7/00	Mine waste 260 μg/g	FC	500	510–910 Night	12 9	$r^2 = 0.97$, $p < 0.05$ $r^2 = 0.47$, $p < 0.05$
DRI Ecocells, Reno, NV 11/17–21/00	Tailings amended soil 12 μg Hg/g	FC	615	Date 415–940/all light data/night 17th 33.4/22.4/13.44 18th 30.9/23.8/17.5 19th 23.6/18.8/8.7 20th 32.3/26.9/22.9 21st 31.1/28.9/32 All data r2 > 0.63, p < 0.05		
Tahquamenon River Watershed, MI	Background soils	FC		29.4 (Zhang et al., 2001)		
Walker Branch Watershed, TN		UMet		17.3–25.8 (Kim and Lindberg, 1995)		
Watson Forest, E. TN		FC		18.0–24.9 (Carpi and Lindberg, 1998)		
St. Anicet, S. Quebec		FC		20.5 (Poissant and Casimir, 1995)		

available while in situ derived data was influenced by visible light and light in the ultraviolet realm. Zhang et al. (2001) demonstrated that ultraviolet light was important but not solely responsible for influencing light-enhanced emissions.

Photo-induced Hg emissions from substrate were found to occur from synthetic HgS, and Hg^0 and $HgCl_2$ amended substrates containing iron oxide and organic phases. All Hg enriched natural substrates used in this study exhibited light enhancement of Hg emissions above that occurring in the dark at the same temperature. Phases that appear to be associated with photo-reduction include cinnabar, mHgS, matrix bound Hg and the mineral corderoite. Light-enhanced emissions from substrate were higher from substrate identified to have mHgS, matrix bound Hg, and corderoite. Calculated activation energies indicate that photo-reduction of Hg-phases is an important process associated with emissions from both synthetic and natural Hg containing substrates.

Based on in situ derived data, photo-reduction of Hg phases and/or energy intensive physical desorption of Hg bound to other phases is/are important processes associated with the release of Hg especially with first light. After a pool of available Hg^0 is developed, gaseous Hg^0 release becomes a dominant process facilitated by

increasing soil temperatures and convective heat transfer occurring during the day.

These results have important implications for development of models for scaling up Hg emissions from naturally enriched and background areas. To truly characterize area emissions spatially and temporally the influence of light on emissions from substrate needs to be included.

Acknowledgements

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